

SURFACE EVOLUTION CAUSED BY SUB-SURFACE DEFECT DYNAMICS

Many processes change the chemical composition at surfaces and interfaces. Corrosion and evaporation can change the composition at surfaces, while the motion of atoms can do the same where two materials are joined. These changes affect the local topology and can change radically how materials function, causing desirable properties to degrade over time. For this reason, it is important to ask: How do surfaces respond, at the atomic scale, to local changes in composition? What are the microscopic mechanisms by which atoms are transported and new chemical phases nucleate?

We observed directly how the surface of an alloy changes when exposed to a flux of one of its components. While exposing a nickel-aluminum (NiAl) crystal to aluminum (Al) atoms, we used low-energy electron microscopy (LEEM) to follow the surface's response in real time, and at the atomic-layer scale. LEEM is a powerful technique that enables us to create movies of dynamic processes that occur on the topmost atomic layers of a material. A frame from a LEEM movie is shown in Figure 1(a). The image is like a contour map of the surface. The dark lines divide regions of the surface that differ in height by a single atomic layer. Relative heights are indicated as "low," "high," and "higher" in the image. In this image, a contour line comes to an end at a point marked "D." At this special point, a defect called a dislocation comes to the surface from below. There, the first and second atomic layers have bent in such a way that they come together. During Al deposition on the surface, we observed several surprising phenomena, including changes in the surface topology caused by the motion of such defects.

The composition of our crystal was initially Ni_{0.57}Al_{0.43}, with excess nickel (Ni) atoms residing at "anti-sites," or sites that should be occupied by Al atoms. Upon depositing Al at high substrate temperatures (> 600 K), we immediately observed behavior that was strikingly different from conventional film growth. New NiAl layers appeared on the surface even though only Al was deposited, indicating the substrate was "soaking up" Al and rejecting Ni. Quantitative measurements showed that initially, half of the incident Al flux went into the bulk, or sub-surface, to replace excess Ni atoms. The other half reacted with Ni that was rejected by the bulk to form new alloy on the surface. The growth of NiAl on the surface can be seen by comparing Figures 1(a), 1(b), and 1(c). The steps in Figure 1(a) "flowed" toward lower terraces and new islands appeared. At this stage, the alloy growth was fueled entirely by the incoming Al and the diffusion of excess Ni atoms from anti-sites.

However, this atom exchange, which replaced Ni anti-sites in the bulk with Al atoms from the surface, did not continue

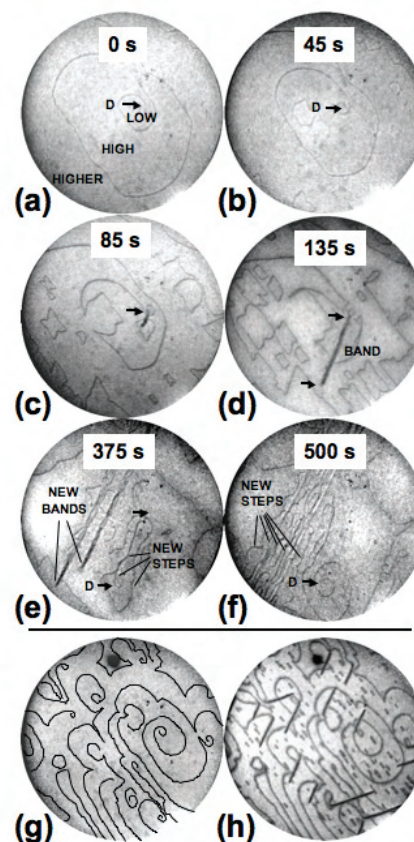


Figure 1. Evolution of the NiAl(110) surface exposed to an Al flux. (a) 5 μm diameter area on the clean (110) surface before exposure to the Al flux. (b) The terraces advance as new NiAl grows above the original surface. (c) Dark contrast appears at the dislocation. (d) The dark band elongates linearly across the surface. (e) The dark band vanishes, revealing that the dislocation moved to its endpoint. Two new bands from dislocations outside of the field of view move linearly across the surface. (f) Growth of NiAl terraces proceeds and the dislocation remains at its new location. (g) LEEM image of a 25- μm area with a high density of dislocations that terminate at the surface. (h) LEEM image of the same area after deposition of < 1 monolayer of Al at 700 K.

indefinitely. Once the excess Ni was consumed, new NiAl layers had to form by "stealing" Ni from Ni sites. In this way, Al deposition eventually led to a build-up of Ni vacancies in the near-surface region. When those vacancies were sufficiently abundant, they condensed at dislocations and made them move, leaving dark bands [Figures 1(c-h)] in their wakes. The condensation of Ni vacancies (which can also be viewed as the removal of Ni atoms) changed the composition of the crystal along these bands.

We have elucidated a detailed alloying mechanism. The dislocations dissociate into partial dislocations that climb across the surface due to Ni vacancy condensation (Ni atom removal) and leave faults of an Al-rich phase behind. Instead of developing into stable nuclei of an Al-rich phase, the

faults eventually collapse, as in Figure 1(d-e). The net result of the dislocation motion and fault formation is to enhance the transport of Al (Ni) from the surface (bulk) to the bulk (surface) over that possible by point defect action alone.

We found that phenomena typically thought of as bulk processes could dictate mass transport and chemical changes at surfaces. We learned that dislocations and point defects, which are ubiquitous “bulk” features in solids, can critically affect how a surface evolves. During Al deposition on NiAl, these effects were not subtle, but actually governed the motion and creation of atomic steps and the creation of chemical inhomogeneities (the dark bands in Figure 1). The behavior we observed is reminiscent of well-known processes that change the composition in the bulk of alloys via precipitation (i.e., Guinier-Preston zone formation and Suzuki segregation). The dynamics of these processes, however, had been seldom directly observed and their effects on materials’ surfaces had not been appreciated until now.

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John Pierce earned a Ph.D. in physics from the University of Tennessee with his work on tailoring ultra-thin magnetic nanostructures on surfaces. He joined Sandia as a post-doctoral fellow in 2003 and is currently in Micro & Interfacial Sciences Dept. 8756. His main research interests lie in understanding the dynamics of atoms on surfaces and how they can be controlled to create functional structures. He is an avid snowboarder, hiker, and cage fighter.